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ON THE AMOUNT OF OXYGEN AND CARBONIC ACID
DISSOLVED IN NATURAL WATERS AND THE
EFFECT OF THESE GASES UPON THE
OCCURRENCE OF MICROSCOPIC
ORGANISMS

BY GEORGE C. WHIPPLE AND HORATIO N. PARKER

WITH FOUR PLATES

INTRODUCTION

Of the many factors which affect the growth of microscopic organisms in water the most important is their food supply, and of the elements which enter into their composition oxygen and carbon are of fundamental importance. Ordinarily these two elements are not determined in the sanitary analysis of water, and data on their occurrence in natural waters are not as numerous as one could wish; and especially there are lacking parallel observations upon the amount of carbonic acid and the number of the microscopic organisms. With nitrogen the case is different. This element plays a conspicuous part in sanitary water-analysis, and the relation between the amount of nitrogen as it exists in various states and the microscopic organisms present in the water has been carefully worked out.

Nitrogen is usually determined in four states: First, as "albuminoid ammonia," that is, nitrogen existing as organic matter; second, as "free ammonia," which represents the preliminary stage of decomposition of the organic matter; third, as "nitrites," which represent a further stage in decomposition; and, fourth, as "nitrates," which represent the final stage of decomposition, that of complete mineralization. Nitrogen exists also as a gas dissolved in the water, but as such it is seldom determined. It seems to have been taken for granted, and apparently with good reason, that dissolved nitrogen is as inert in its relations with organic life as is the nitrogen of the atmosphere; but it has been discovered that some forms of

terrestrial plant life, aided by the action of certain bacteria, are able to utilize atmospheric nitrogen, and it may be that aquatic plants can in like manner assimilate dissolved nitrogen. The relations that exist between algae growths and the nitrogen contents of water as ordinarily determined are illustrated by Plate XIX.

SOLUBILITY OF OXYGEN AND CARBONIC ACID

Great variations exist in the solubility of gases in water. At 20° C. one liter of water has the power of absorbing 28.38 c.c. of oxygen, 14.03 c.c. of nitrogen, 901.4 c.c. of carbonic acid, and 654,000 c.c. of ammonia. The coefficient of absorption of a gas is the volume of that gas—expressed in cubic centimeters and measured at 0°C. under a pressure of 760 mm. of mercury—which is dissolved in 1 c.c. of water. Except in the case of hydrogen, the coefficient varies with the temperature, decreasing as the temperature increases. The coefficients of absorption at various temperatures for oxygen, nitrogen, and carbonic acid are given in the following table:

TABLE I
COEFFICIENTS OF ABSORPTION OF VARIOUS GASES, AFTER BUNSEN¹

TEMPERATURE (Centigrade)	OXYGEN	NITROGEN	CARBONIC ACID
0	0.04114	0.02035	1.7967
1	0.04007	.01981	1.7207
2	.03907	.01932	1.6481
3	.03810	.01884	1.5787
4	.03717	.01838	1.5126
5	.03628	.01794	1.4497
6	.03544	.01752	1.3901
7	.03465	.01713	1.3339
8	.03389	.01675	1.2809
9	.03317	.01640	1.2311
10	.03250	.01607	1.1847
11	.03189	.01577	1.1416
12	.03133	.01549	1.1018
13	.03082	.01523	1.0653
14	.03034	.01500	1.0321
15	.02989	.01478	1.0020
16	.02949	.01458	.9753
17	.02914	.01441	.9519
18	.02884	.01426	.9318
19	.02858	.01413	.9150
20	.02838	.01403	.9014

¹Gasometrische Methoden, Braunschweig. 1877.

The volume of the gas dissolved is the same, whatever the pressure, but inasmuch as the density of the gas increases directly with the pressure, it follows that the actual quantity of the gas dissolved varies directly with the pressure. In the case of a mixture of the gases, the quantity of any one of them which will be dissolved depends upon the vapor pressure of that particular gas, regardless of the others. Thus, water at 0° C. will dissolve 41.14 c.c. per liter of oxygen if exposed to an atmosphere of pure oxygen under 760 mm. pressure, but if exposed to the air, which is but one-fifth oxygen, it will absorb 41.14 c.c. of oxygen under one-fifth the pressure; consequently only one-fifth as much by weight as in the first case. Again, water at 0° will dissolve 901.4 c.c. per liter of carbonic acid in an atmosphere of that gas under 760 mm. pressure, while in the air of a room where the amount of carbonic acid is only 0.2 per cent, the amount dissolved will be only one-five-hundredth of that quantity by weight. This law is said to be only approximately true in the case of gases which form but a small per cent of any mixture of gases.

The coefficient of absorption of oxygen is greater than that of nitrogen; consequently when water is exposed to air it will absorb a larger amount of the former gas. Bunsen has given the following figures to illustrate this:

	COMPOSITION OF AIR BY VOLUME	COMPOSITION OF DISSOLVED AIR BY VOLUME
Oxygen	20.96 per cent	34.91 per cent
Nitrogen	79.04 per cent	65.09 per cent
	100.00 per cent	100.00 per cent

It is possible for water to temporarily contain a larger amount of gas than it will actually dissolve under definite conditions of temperature and pressure; that is, it may be supersaturated. Thus, after violent agitation, as in passing over a fall, oxygen may become mechanically entrained, and a sample taken immediately may show an amount several per cent above what normally would be expected. "Soda water," which is water charged with carbonic acid under pressure, is an exaggerated case of supersaturation. On exposure to ordinary atmospheric conditions a supersaturated water gives off gas until equilibrium is established. Sometimes the quantity of gas given off is so minute that it can be measured only by the most delicate chemical methods; at others the action is vigorous enough to become manifest to the eye in the phenomenon of effervescence. Cases of

water supersaturated with carbonic acid are very common. In outdoor air the pressure of carbonic acid is so very low that the amount which is dissolved in water is very small. Ground water usually contains relatively large amounts of carbonic acid, and on exposure to the air yields it up until normal conditions of solution are established. This tendency to equalization makes it necessary to exercise great care in the determination of carbonic acid.

Water may be freed of its dissolved gases to a considerable extent by boiling, but it is only by prolonged boiling in a vacuum that the last traces can be removed. In the early days of water analysis the dissolved gases were driven off in this manner and were collected and measured by the tedious process of gas analysis. The procedure still remains one of the most accurate, but on account of its inconvenience it has been superseded by simpler methods for the determination of dissolved oxygen and carbonic acid.

WINKLER'S METHOD OF DETERMINING THE AMOUNT OF DISSOLVED OXYGEN IN WATER²

Sample.—The sample from which the determination of dissolved oxygen is to be made must be collected with extreme care, as faulty manipulation may easily cause an increase of oxygen by absorption from the air. A glass-stoppered bottle with narrow neck and holding approximately 250 c.c. should be used. The exact capacity of the bottle with the stopper in place should be determined and, for convenient reference, scratched with a diamond upon the glass. The bottle can not be safely filled by pouring the sample into it, nor yet by sinking it in a pond and allowing the air to bubble out; it is necessary that the water enter at the bottom in a gentle current. If the sample is to be collected from a faucet the water must be made to enter the bottle through a glass or rubber tube which reaches to the bottom of the bottle, the water being allowed to overflow for several minutes, after which the glass stopper is carefully pressed home so that no bubble of air is caught beneath it. If the sample is to be collected from a stream or pond the apparatus shown in Fig. 1 should be used.

² *Berichte*, XXI, 2843; 1888. See also Richards and Woodman, *Air, Water, and Food*, p. 107; John Wiley and Sons, 1900, New York. A. H. Gill, *Tech. Quar.*, V, p. 250; 1892. *Special Rept. Mass. St. Bd. of Health on Purification of Sewage and Water*, p. 722; 1890.

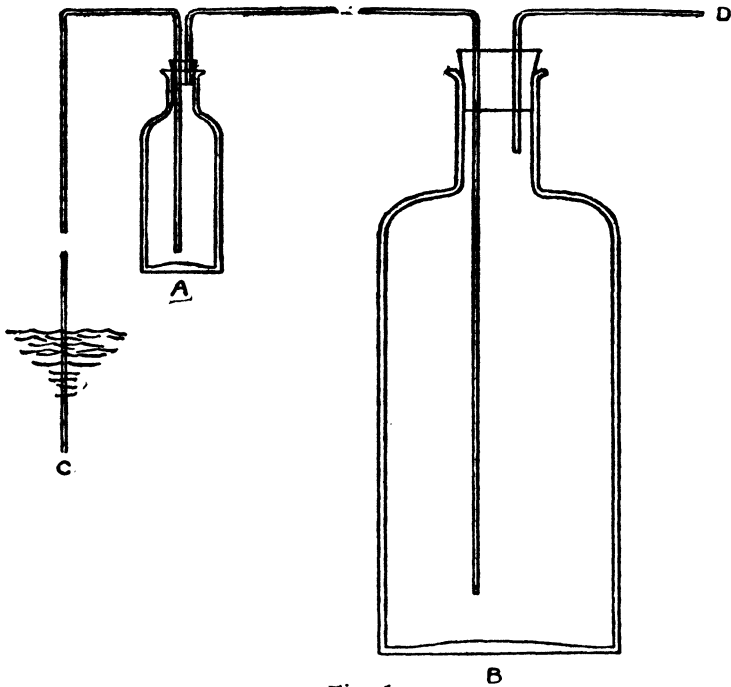


Fig. 1.

The sample bottle, *A*, is provided with a rubber stopper through which pass two tubes, one reaching nearly to the bottom of the bottle and the other terminating at the bottom of the stopper. The longer one is attached to a rubber tube of length sufficient to reach the point where the sample is to be taken; the shorter is attached to the tube of a large bottle, *B*, similarly provided with inlet and outlet. If suction is applied at the point *D* the water will enter at *C*, fill the bottle *A*, and ultimately fill the bottle *B*. The bottle *B* should have several times the capacity of *A*, and water should be drawn through *A* until a fair sample has been secured. If the sample is to be collected from a considerable depth a small lead pipe, which will serve as a weight and will neither collapse nor stretch, may be attached to *C*. It may be marked off in meters showing the depth of the sample. Suction may be secured with the mouth, but it is preferable to use an air pump. As soon as the bottle *A* has been filled with a satisfactory sample the rubber stopper should be removed and the glass stopper

inserted as before. It is always advisable to ascertain the temperature of the sample in order that the results of the determination may be expressed, if desired, in per cent of saturation.

SOLUTION REQUIRED

a. Manganous sulfate solution. Dissolve 48 grams of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in 100 c.c. of distilled water.

b. Solution of sodium hydroxid and potassium iodid. Dissolve 360 grams of NaOH and 100 grains of KI in 1,000 c.c. of distilled water.

c. Hydrochloric acid, sp. gr. 1.20.

d. Sodium thiosulfate solution. Dissolve 24.827 grams of chemically pure recrystallized sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in 1,000 c.c. distilled water. Dilute 100 c.c. of this solution to one liter with distilled water.

This gives a N/100 solution, each cubic centimeter of which is equivalent to .00008 grams of oxygen, or 0.055825 c.c. of oxygen at 0° and 760 mm. pressure. Inasmuch as this solution is not permanent it should be standardized occasionally against a N/100 solution of potassium bichromate as described in almost any work on volumetric chemistry.

e. Starch Solution.—Mix a small amount of clean potato starch with cold water until it becomes a thin paste; stir this into 150 to 200 times its weight of boiling water and continue the boiling for a few minutes; then let it stand and settle. It may be preserved by adding a few drops of chloroform.

METHOD OF PROCEDURE

Remove the stopper from the bottle which contains the sample and with a pipette long enough to reach the bottom of the bottle add approximately 2 c.c. of the manganous sulfate solution. Then, in a similar way, add approximately 2 c.c. of the sodium hydroxid potassium iodid solution. Replace the stopper in such a way as to leave no air bubbles, and mix the contents of the bottle. The manganous sulfate and sodium hydroxid react to form manganous hydroxid, a part of which at once combines with whatever dissolved oxygen is present, to form manganic hydroxid. Allow the precipitate to settle; add about 2 c.c. of strong hydrochloric acid

and mix thoroughly. This reacts with the manganic hydroxid and liberates chlorin, which in turn liberates iodine from the potassium iodid. The amount of iodine liberated therefore depends upon the amount of dissolved oxygen present.

Up to this point the process must be carried on at the time the sample is collected, but after the hydrochloric acid has been added and the stopper replaced, there is practically no further change, and the rest of the operation, which consists of the determination of the amount of iodine, may be conducted at leisure. Thus samples collected in the field are dosed with the three solutions and then taken to the laboratory where the examination is completed.

The amount of liberated iodine is determined as follows:

When the precipitate has nearly dissolved after the addition of the acid, the contents of the bottle are rinsed out into a flask and titrated with a N/100 solution of sodium thiosulfate, using a few cubic centimeters of the starch solution as an indicator. It is best not to add the starch until the color has become a faint yellow. The titration is continued until the blue color has disappeared.

CALCULATION AND EXPRESSION OF RESULTS

There are three ways of expressing the amount of dissolved oxygen in water, namely: In parts per million by weight, in number of cubic centimeters of the gas per liter at 0° and 760 mm. pressure, and in per cent of saturation, that is, the per cent which the amount of gas present is of the amount capable of being dissolved by water at the same temperature and pressure.

The following formulae may be used to ascertain the results according to the three methods:

$$\text{Oxygen in parts per million} = \frac{.00008n \times 1,000,000}{v} = \frac{80n}{v}$$

$$\text{Oxygen in c.c. per liter} = \frac{.055788n \times 1000}{v} = \frac{55.788n}{v}$$

$$\text{Oxygen in per cent of saturation} = \frac{.055788n \times 1000 \times 100}{v \times O} = \frac{5578.8n}{vO}$$

where n = number of c.c. of $\frac{N}{100}$ thiosulfate solution.

v = capacity of the bottle in cubic centimeters less the volume of the manganous sulfate and potassium iodid solution added (i. e., less 4 c.c.).

O=the amount of oxygen in c.c. per liter in water saturated at the same temperature and pressure. See Table II.

TABLE II

AMOUNT OF DISSOLVED OXYGEN IN DISTILLED WATER WHEN SATURATED AT DIFFERENT TEMPERATURES FROM 0° TO 30° C.³ (PREPARED BY ROSCOE AND LUNT. SEE JOUR. CHEM. SOC., P. 552, 1839. SEE ALSO SUTTON'S VOLUMETRIC ANALYSIS, P. 275)

TEMPERATURE (Centigrade)	NO. OF C.C. OF OXYGEN PER LITER OF WATER	LOGARITHM OF NUMBERS	TEMPERATURE (Centigrade)	NO. OF C.C. OF OXYGEN PER LITER OF WATER	LOGARITHM OF NUMBERS
0.0	9.70	.986772	16.0	6.82	.833784
0.5	9.60	.982271	16.5	6.75	.829304
1.0	9.49	.977266	17.0	6.68	.824776
1.5	9.38	.972203	17.5	6.61	.820201
2.0	9.28	.967548	18.0	6.54	.815578
2.5	9.18	.962843	18.5	6.47	.810904
3.0	9.08	.958086	19.0	6.40	.806180
3.5	8.98	.953276	19.5	6.34	.802089
4.0	8.87	.947924	20.0	6.28	.797960
4.5	8.78	.943495	20.5	6.22	.793790
5.0	8.68	.938520	21.0	6.16	.789581
5.5	8.58	.933487	21.5	6.10	.785330
6.0	8.49	.928908	22.0	6.04	.781037
6.5	8.40	.924279	22.5	5.99	.777427
7.0	8.31	.919601	23.0	5.94	.773786
7.5	8.22	.914872	23.5	5.89	.770115
8.0	8.13	.910091	24.0	5.84	.766413
8.5	8.04	.905256	24.5	5.80	.763428
9.0	7.95	.900367	25.0	5.76	.760422
9.5	7.86	.895423	25.5	5.72	.757396
10.0	7.77	.890421	26.0	5.68	.754348
10.5	7.68	.885361	26.5	5.64	.751279
11.0	7.60	.880814	27.0	5.60	.748188
11.5	7.52	.876218	27.5	5.57	.745855
12.0	7.44	.871573	28.0	5.54	.743510
12.5	7.36	.866878	28.5	5.51	.741152
13.0	7.28	.862131	29.0	5.48	.738781
13.5	7.20	.857332	29.5	5.45	.736397
14.0	7.12	.852480	30.0	5.43	.734800
14.5	7.04	.847573	30.5	5.40	.732394
15.0	6.96	.842609	31.0	5.38	.730782
15.5	6.89	.837588			

For example, suppose the capacity of the bottle to be 264.5 c.c., the temperature of the water to be 10° C., and suppose that 28.6 c.c.

³ Below 5° the results are extrapolated and are not strictly accurate. The results given are calculated for aeration at an observed pressure of 760 mm. When the observed pressure is below 760 mm. $\frac{1}{76}$ the value must be subtracted for every 10 mm. difference; and when the observed pressure is above 760 mm. a like amount must be added.

$\frac{N}{100}$ thiosulfate were used in the titration. Then

$$\text{Oxygen in parts per million} = \frac{80 \times 28.6}{260.5} = 8.78$$

or,

$$\text{Oxygen in c.c. per liter} = \frac{55.788 \times 28.6}{260.5} = 6.12$$

or,

$$\text{Oxygen in per cent of saturation} = \frac{5578.8 \times 28.6}{260.5 \times 7.77} = 78.7 \text{ per cent.}$$

The labor of calculation may be diminished by the use of logarithms. Furthermore, inasmuch as $\frac{80}{v}$ in the first equation, $\frac{55.788}{v}$ in the second, and $\frac{5578.8}{v}$ in the third are constants for any particular bottle, it is convenient to have in a note-book, or upon the bottles themselves, the logarithms of these quantities. It is also desirable to bear in mind the following data:

1 c.c. of oxygen at 0° and 760 mm. pressure weighs .001434 g.

1 c.c. $\frac{N}{100}$ thiosulfate solution = .00008 g. = .055788 c.c.

0.7 c.c. oxygen per liter = 1 part per million by weight (approximately).

1 c.c. oxygen per liter = 1.43 parts per million by weight (approximately).

1 cu. ft. oxygen = 40.6 g.

1 gallon oxygen = 5.52 g.

SOURCES OF ERROR

It is necessary to correct for the manganous sulfate and for the potassium iodid-sodium hydrate solution added, but if the precipitate is allowed to settle before the acid is added it is not necessary to correct for the latter, as the water displaced has already given up its oxygen.

In practice perhaps the greatest source of error is carelessness in collecting the sample, thus allowing atmospheric air to become entrained. This is particularly the case when the amount of oxygen is small. Supersaturation with oxygen, however, seldom occurs.

To some extent the amount of organic matter interferes with the

result by exerting a reducing action, and high nitrates, also, materially affect the result. These sources of error are discussed in Winkler's paper; in actual practice it is seldom necessary to take them into account. Neither is it necessary to correct for atmospheric pressure when expressing the results in number of cubic centimeters per liter.

METHOD OF DETERMINING THE AMOUNT OF CARBONIC ACID IN WATER

Although water has a large capacity for absorbing carbonic acid, as stated above, yet the pressure of the carbonic acid in the air is so small that under ordinary atmospheric conditions the amount dissolved is very slight. When water which contains carbonic acid comes in contact with the carbonates of calcium and magnesium it is supposed to unite with them to form the bicarbonates of these metals,—salts which are readily soluble. The normal carbonates, themselves, but are slightly soluble. If the amounts of the normal carbonates are in excess, all of the dissolved carbonic acid will be used up, but if the carbonic acid is in excess the quantity of it remaining in solution will be proportional to the pressure of the carbonic acid in the atmosphere. Inasmuch as most surface and ground waters come in contact with the carbonates of the alkaline earths during some part of their history, it follows that natural waters ordinarily contain carbonic acid in three different conditions. That part which simply remains in solution uncombined with any base is termed the "free carbonic acid"; if it is combined directly with the bases to form the normal carbonates (CaCO_3 and MgCO_3) it is called the "fixed, or full-bound carbonic acid"; while if it is combined indirectly with the normal carbonates to form the bicarbonates it is known as the "half-bound carbonic acid." The sum of the three gives the total carbonic acid. When water which contains carbonic acid in these three forms is heated the free and half-bound carbonic acid is given off, and is sometimes referred to as the volatile carbonic acid.

In the analysis of water for sanitary or industrial purposes it is sometimes necessary to ascertain the amount of carbonic acid in each of the three forms, but in the study of biological problems it is chiefly the free carbonic acid which is involved. Various methods have been suggested for the determination of the carbonic acid. These have been recently discussed in an excellent paper by Ellms and Beneker

in the *Journal of the American Chemical Society*, Vol. XXIII, No. 6 (June, 1901), to which the reader is referred.

The free carbonic acid may be easily determined by titration with a solution of sodium carbonate, using phenolphthalein as an indicator. As soon as the sodium carbonate has combined with all the free carbonic acid present, with the formation of bicarbonate of soda, any further addition will produce a pink color. In case there is no free carbonic acid present the phenolphthalein will produce a pink color when the first drop of sodium carbonate is added, or even before it is added at all. The details of the method as practiced by the authors are as follows:

Sample.—If the determination can not be made at the time the sample is collected, the bottle should be filled completely, without leaving any air space under the stopper. It is preferable to collect the sample in the receptacle in which the titration is to be made. The required solutions are prepared as follows:

Sodium Carbonate Solution ($\text{Na}_2\text{CO}_3 \frac{\text{N}}{22}$).

A normal solution of sodium carbonate is first made by dissolving 53 g. of the freshly fused, chemically pure salt in one liter of freshly boiled distilled water. This should be kept in a hard glass bottle with glass stopper. The $\frac{\text{N}}{22}$ solution used in the titration is made from this by dilution with boiled distilled water. As this solution easily absorbs carbonic acid from the air and thereby changes to bicarbonate, it is important that it be exposed to the air as little as possible. It is even advisable to supply the burette by side connection with the supply-bottle and to provide tubes filled with caustic lime upon both the supply bottle and burette, in order that the carbonic acid may be removed from the air before it comes in contact with the solution. The burette should be graduated to 0.1 c.c.

Phenolphthalein Indicator.

This is prepared by dissolving 0.5 g. of the powdered salt in 100 c.c. of 50 per cent alcohol. A few drops of a weak solution of sodium hydrate should be cautiously added until a faint pink color is found, which just disappears after shaking. For use this may be kept in a small glass-stoppered bottle with a pipette stopper.

Mode of Procedure.—The determination is made by putting 100 c.c. of the sample in a 100 c.c. Nessler tube with 10 drops of the phenolphthalein indicator. The sodium carbonate solution is then

added from a burette and stirred until the faint pink color which appears remains permanent. The difference between the burette readings before and after titration expressed in tenths of a cubic centimeter gives the amount of carbonic acid in parts per million. For example, if the burette readings are 31.3 and 32.9, the difference is 1.6, and the corresponding amount of carbonic acid is 16 parts per million. If due precautions are taken the results should be correct to about one part in a million.

The greatest sources of error in the method come from the loss of carbonic acid to the air and from the absorption of carbonic acid by the solution of sodium carbonate. The latter may be prevented by adopting the precautions described above, while the former may be reduced to a minimum by making the titration as soon as possible after collection, and by collecting the sample in the tube in which the titration is to be made. Great care should be used in stirring the solution. In fact, instead of stirring, it is often better to mix the added solution by rapidly whirling the tube in such a way that it describes the surface of a cone. If a stirring rod is used it should be bent so that at the lower end there is a circle with its plane at right angles to the rod.

Exposure to the air ordinarily results in loss of free carbonic acid, which may be illustrated by the following experiment:

A series of samples was collected and carbonic acid determinations made in the field, while a corresponding series was collected and sent to the laboratory, where determinations were made at the end of twenty-four hours. A third series was allowed to stand the same length of time, but without being stoppered. The results were as follows:

	AMOUNT OF CARBONIC ACID IN PARTS PER MILLION		
	Determination made at the time of collection	Determination made after standing 24 hours with tube completely filled and stoppered	Determination made after standing 24 hours with water exposed to the air
Surface water No. 1.....	8.8	9.0	1.5
Surface water No. 2.....	1.3	1.5	0.5
Surface water No. 3.....	0.5	0.5	0.5
Ground water No. 1.....	7.0	6.5	1.5
Ground water No. 2.....	7.0	7.0	1.0
Ground water No. 3.....	7.0	7.0	1.0
Ground water No. 4.....	2.5	2.0	-1.0

At another time carbonic acid gas was passed through distilled water until the water contained 45.5 parts per million. Portions of 200 c.c. were then put in completely filled, tightly stoppered bottles, and in open bottles exposed to the air at different temperatures. The results were as follows:

	AMOUNT OF CARBONIC ACID (PARTS PER MILLION)		
	At beginning of experiment	After standing 3 hours	After standing 20 hours
Bottle filled and tightly stoppered.....	45.5	44.0	44.5
Bottle unstoppered, temperature 17.0° C.	45.5	26.0	0.5
Bottle unstoppered, temperature 20.0° C.	45.5	23.5	0.5
Bottle unstoppered, temperature 37.0° C.	45.5	15.0	0.3

Thus in less than twenty-four hours practically all of the carbonic acid had been given off to the air.

It is not even necessary that the bottle shall be unstoppered in order that a loss of carbonic acid may occur. If the bottle is only partially filled, there oftentimes will be a loss to the air in the bottle. Thus a water which contained 15 parts of carbonic acid per million was distributed into half-filled 8-oz. bottles. The first bottle was tested at the end of twenty-four hours; the second at the end of forty-eight hours, and so on, with the following results:

	AMOUNT OF CARBONIC ACID
At beginning.....	15.0
At end of 24 hours.....	13.5
At end of 48 hours.....	8.0
At end of 72 hours.....	2.5
At end of 96 hours.....	1.8

The danger of loss of carbonic acid while pouring the sample back and forth through the air is illustrated by the following experiment: Carbonic acid was passed through water until 63 parts per million were dissolved. A portion of the water was then poured back and forth four times and tested. It was found to contain 57.5 parts, showing a loss of 9 per cent.

The amount of carbonic acid given up in this way depends in part upon the pressure of the carbonic acid in the air. On exposure to the air a sample of boiled distilled water will absorb from it a certain amount of carbonic acid. Out of doors this is seldom greater than

0.5 parts per million, but in the air of a laboratory, when gas is used freely, it sometimes amounts to 1.5 or even 3.0 parts. Ellms and Beneker mention an instance where it was 15 parts per million, but in this case a carbonic acid generator was in use in the laboratory.

There is, in short, a tendency for the carbonic acid in the air and in the water exposed to the air to come to an equilibrium. This must occur in natural bodies of water as well as in small samples, and it doubtless plays an important part in the economy of nature.

It sometimes happens that there is no free carbonic acid present, in which case the water is neutral to phenolphthalein; or the water may be alkaline to phenolphthalein, showing that some of the carbonates are in solution as normal carbonates instead of as bicarbonates.

If it is desired to obtain the amount of carbonic acid in the three states mentioned, a second titration should be made with $\frac{N}{50}$ H_2SO_4 , using methyl orange (cold), or preferably lacmoid (hot) as the indicator.

It is best to express the results of all chemical analyses of water in parts per million, that is, in milligrams per liter, but in case it is desired to express the amount of carbonic acid in cubic centimeters per liter, the following table⁴ will be found convenient:

TABLE III

WEIGHT IN MILLIGRAMS OF A CUBIC CENTIMETER OF CARBONIC DIOXID FROM 746 TO 778 MILLIMETERS PRESSURE AND FROM 10° TO 25° C. CORRECTED FOR THE TENSION OF AQUEOUS VAPOR.

Temper- ature	MILLIMETERS																
	746	748	750	752	754	756	758	760	762	764	766	768	770	772	774	776	778
10°	1.839	1.844	1.849	1.854	1.859	1.864	1.869	1.874	1.879	1.884	1.889	1.894	1.899	1.904	1.909	1.914	1.919
11	1.831	1.836	1.841	1.846	1.851	1.856	1.861	1.866	1.871	1.876	1.881	1.886	1.891	1.896	1.901	1.906	1.911
12	1.823	1.828	1.833	1.838	1.843	1.848	1.853	1.858	1.863	1.868	1.873	1.878	1.883	1.888	1.893	1.898	1.903
13	1.815	1.820	1.825	1.830	1.835	1.840	1.845	1.850	1.855	1.860	1.865	1.870	1.875	1.880	1.885	1.889	1.894
14	1.807	1.812	1.817	1.822	1.827	1.832	1.837	1.842	1.847	1.852	1.856	1.861	1.866	1.871	1.876	1.881	1.886
15	1.799	1.804	1.809	1.814	1.818	1.823	1.828	1.833	1.838	1.843	1.848	1.853	1.858	1.863	1.868	1.872	1.877
16	1.791	1.795	1.800	1.805	1.810	1.815	1.821	1.825	1.830	1.835	1.839	1.844	1.849	1.854	1.859	1.864	1.869
17	1.782	1.787	1.792	1.797	1.801	1.806	1.811	1.816	1.821	1.826	1.831	1.836	1.841	1.846	1.851	1.855	1.860
18	1.774	1.779	1.784	1.788	1.793	1.798	1.803	1.808	1.813	1.818	1.823	1.828	1.832	1.837	1.842	1.847	1.852
19	1.765	1.770	1.775	1.780	1.785	1.790	1.794	1.799	1.804	1.809	1.814	1.819	1.823	1.828	1.833	1.838	1.843
20	1.757	1.761	1.766	1.771	1.776	1.781	1.786	1.791	1.795	1.800	1.805	1.810	1.815	1.820	1.825	1.829	1.834
21	1.748	1.753	1.758	1.763	1.767	1.772	1.777	1.782	1.787	1.792	1.797	1.802	1.806	1.811	1.816	1.820	1.825
22	1.739	1.744	1.749	1.754	1.759	1.764	1.769	1.773	1.778	1.783	1.787	1.792	1.797	1.802	1.807	1.811	1.816
23	1.731	1.735	1.740	1.745	1.750	1.755	1.760	1.764	1.769	1.774	1.778	1.783	1.788	1.793	1.798	1.802	1.807
24	1.721	1.726	1.731	1.736	1.741	1.746	1.751	1.755	1.760	1.765	1.769	1.774	1.779	1.784	1.789	1.793	1.798
25	1.713	1.718	1.722	1.727	1.732	1.737	1.741	1.746	1.751	1.756	1.760	1.765	1.770	1.775	1.780	1.784	1.789

⁴Ellen H. Richards and Alpheus G. Woodman, *Air, Water, and Food*, p. 196. John Wiley & Sons, New York, 1900.

AMOUNT OF OXYGEN IN NATURAL WATERS UNDER VARIOUS
CONDITIONS

The oxygen dissolved in water is derived primarily from the atmosphere. If distilled water, freed of oxygen by boiling, stands exposed to the air it absorbs oxygen and in a few hours becomes saturated, or, to use the popular expression, aerated. This is accomplished even more quickly if the water falls through the air in drops. Roscoe and Lunt obtained the standard aerated water used in the preparation of Table II as follows: Two glass-stoppered quart bottles were half-filled with distilled water and shaken for five minutes, the air being renewed several times by filling one bottle with the contents of the other and dividing it again into two portions. Finally one bottle being filled, the temperature was taken and also the barometric pressure, after which the bottle was allowed to stand stoppered for half an hour to get rid of minute air bubbles. Roscoe and Lunt's figures are probably somewhat more accurate than those given by Bunsen and Winkler.

In the case of natural waters exposed to sunlight there is another source of oxygen, namely aquatic vegetation. It is a well-known fact that chlorophyllaceous plants exposed to sunlight exhale oxygen. This is true of aquatic as well as terrestrial plants, and of the microscopic organisms as well as the larger forms. Several years ago T. Chalkley Palmer⁵ described an interesting method for demonstrating this fact in the case of the diatom *Eunotia major*, Rabenhorst. It was based upon the color changes produced in hematoxylin by carbonic acid and oxygen. When this indicator is dissolved in water which contains oxygen it has a rosy pink color, but if one breathes into the solution through a glass tube the color will change to a light brown. If now the solution be poured back and forth from one beaker to another the pink color will return, because the carbonic acid will have been liberated and oxygen acquired. Palmer placed his growing diatoms in a test tube provided with a capillary tube which passed through the stopper. The test tube was held inverted with the capillary point under the surface of a jar of water. The water was first colored pink by the addition of a watery solution of hematoxylin. The color was then changed to a light brown by

⁵ *Proc. Acad. of Nat. Sci. of Philadelphia*, p. 142. Feb., 1897.

charging the water with carbonic acid from the lungs. The apparatus was then exposed to sunlight, and in the course of fifteen minutes or half an hour the color of the liquid in the test tube had become pink because of the liberation of oxygen by the growing diatoms. Later the color became a brilliant red.

M. Albert-Levy, Directeur du Service Chimique, l'Observatoire de Montsouris, Paris, has also observed that if samples of water containing algae are kept exposed to sunlight the amount of dissolved oxygen will be increased, and he cites an example where water from the Vanne, which at the time of collection contained 11.1 parts per million, after nine days was found to contain 20.2 parts per million, and after sixty days 39.7 parts. If these figures are correct we have here an example of supersaturation.

While plant life and the atmosphere are supplying oxygen to surface waters, other forces are at work consuming it. All forms of aquatic animal life, both large and small, require oxygen, and most bacteria are likewise dependent upon it. Some oxygen besides is used up without the direct intervention of vital processes in the direct oxidation of organic matter. The fact that minute animal organisms, such as snails, crustacea, rotifera, etc., use up oxygen may be illustrated by placing them in one of Palmer's tubes and noting the change in color of the hematoxylin solution from red to brown. The exhaustion of oxygen by a culture of bacteria in a hermetically sealed jar may be also shown by the use of this indicator. The fact that decomposition of organic matter is accompanied by loss of dissolved oxygen has given rise to the so-called "incubation test" for determining the quality of water. The sample, which must completely fill the bottle, is kept for several days in the dark at a temperature favorable to rapid bacterial development, and the amount of dissolved oxygen determined before and after the incubation. The greater the amount of organic matter present and the larger the number of bacteria in the original water, the more rapid will be the exhaustion of the oxygen. M. Albert-Levy found that a sample of water from the river Seine which, when collected, contained 10.6 parts per million of dissolved oxygen, lost all of its oxygen after standing fifteen days. While this test is too crude and too inconvenient to be of practical use, it is interesting as an illustration of the point in question. In general, therefore, it may be said that decomposition of organic matter in water means loss or even exhaustion of dissolved oxygen.

Surface waters which contain but little organic matter and which are exposed to the air are usually saturated or almost saturated with oxygen. This is equally true of running brooks, large streams, small pools, and the surface strata of large lakes. Such waters seldom contain less than 80 per cent of the amount required to saturate them. Even if saturated, however, the actual amount of oxygen present varies considerably at different seasons on account of the effect of temperature upon the solubility. This is illustrated in one of the diagrams on Plate XX, which shows the seasonal changes in the temperature of surface waters at Boston, Mass., and the corresponding changes in the amount of oxygen present in a fully saturated water. (See Table IV.) Gill⁶ has shown that at times natural waters may be supersaturated with oxygen, and the same fact has been observed elsewhere. Horton⁷ has stated that in certain streams the water is normally supersaturated during the months of July and August, and he attributes this to the influence of growing plants.

TABLE IV

TABLE SHOWING THE AMOUNT OF OXYGEN IN WATER
WHEN SATURATED AT DIFFERENT SEASONS OF THE
YEAR AT BOSTON, MASS.

MONTHS	AVERAGE TEM- PERATURE, CENTIGRADE	AMOUNT OF OXYGEN	
		No. of cubic centimeters per liter	Parts per million
January	3.7	8.92	12.8
February	3.4	9.01	12.9
March	3.8	8.90	12.7
April	7.4	8.24	11.8
May	13.6	7.19	10.3
June	19.1	6.39	9.1
July	22.0	6.04	8.6
August	22.1	6.03	8.5
September ...	20.0	6.28	9.0
October	14.5	7.04	10.0
November	10.4	7.69	11.0
December	6.7	8.38	12.0

If water contains much organic matter, bacterial decomposition may take place, especially during warm weather. This results in the

⁶(I. c.)

⁷Second report of an investigation of the rivers of Ohio by the State Board of Health 1899.

reduction of the oxygen or even in its entire disappearance. Shallow ponds with muddy bottoms or stagnant pools and sluggish streams with an excess of aquatic vegetation often lose their oxygen during the summer. Sewage, which is very rich in organic matter, loses its oxygen in a very few hours, after which putrefaction sets in. When sewage is allowed to enter a stream the dissolved oxygen is reduced by an amount corresponding to the strength of the sewage and the ratio of its volume to that of the stream. The Merrimac River receives the sewage of the city of Lowell, besides that of other cities, and although the volume of the stream is large, the diminution in the amount of dissolved oxygen in the water at Lawrence, nine miles down stream, is marked. Table V gives by months the per cent of saturation of the water at Lawrence for the years 1893-95. It will be observed that during the summer months there was a material reduction in the amount of oxygen. One of the diagrams on Plate XX shows the effect of the sewage of Paris upon the water of the river Seine. At Choisy-le-Roi, above the entrance of the large sewers, the water is almost saturated for the greater part of the year, and even in summer does not fall far short of saturation; but at Argenteuil, below the city, the amount of oxygen is at all times below that of saturation, and during the summer it is almost exhausted. The same fact is illustrated by Table VI, which shows the progressive diminution of the amount of oxygen between the two stations named, and in parallel series the increasing foulness of the river as illustrated by the chlorin, the organic matter, and the disappearance of oxygen during the forty-eight hours' incubation at 33° C.

TABLE V

TABLE SHOWING THE AMOUNT OF DISSOLVED OXYGEN IN THE WATER OF THE MERRIMAC RIVER AT LAWRENCE, EXPRESSED IN PER CENT OF SATURATION

	JAN.	FEB.	MAR.	APR.	MAY	JUNE	JULY	AUG.	SEPT.	OCT.	NOV.	DEC.
1893.....	91	96	91	100	86	75	52	69	81	86	95	98
1894.....	57	67	76	74	67	58	44
1895.....	83	82	79	98	88	62	59	55	50	68	99

TABLE VI

TABLE SHOWING THE AMOUNT OF DISSOLVED OXYGEN AT VARIOUS STATIONS ON THE RIVER SEINE ABOVE AND BELOW THE CITY OF PARIS. AVERAGE OF TEN YEARS' OBSERVATION BY M. ALBERT-LEVY

STATION	DISSOLVED OXYGEN IN PARTS PER MILLION			ORGANIC MATTER	CHLORIN
	At time of collection of sample	After 48 hours at 33° C.	Per cent used up during in- cubation		
Choisy-le-Roi	10.4	7.8	25	3.1	6.0
Usine d'Ivry	10.8	8.8	18	2.8	7.0
Usine d'Austerlitz	10.7	8.4	21	2.9	7.0
Usine Chaillot	10.0	7.5	25	2.5	7.0
Usine de Suresnes	8.6	5.3	38	3.1	8.0
Usine d'Argenteuil	6.5	2.4	63	4.5	11.0

The amount of dissolved oxygen in large bodies of water varies with the depth. Many observations illustrating this fact are given in Table VII. Near the surface and as far down as the water is kept in circulation by the wind the per cent of saturation is usually above 80 and is often 100, while in the stagnant portion of the water below the thermocline the oxygen diminishes toward the bottom, sometimes gradually and sometimes suddenly. This exhaustion of oxygen has been fully discussed in the reports of the Massachusetts State Board of Health, the Boston Water-works, and elsewhere.⁸ During the winter, as in the summer, there is an exhaustion of oxygen at the bottom of stagnant lakes and often a partial exhaustion at the surface immediately under the ice. This is illustrated by figures given in Table VII. The extent to which the oxygen is used up at the bottom of deep lakes depends chiefly upon the condition of the soil at the bottom. If it is clean sand or gravel the water may remain at least partially aerated for a long time even though the lake is thermally stratified, but if there is a deposit of organic matter decomposition sets in and robs the water of its oxygen.

⁸ See *Microscopy of Drinking Water* by G. C. Whipple. John Wiley & Sons, New York.

TABLE VII

TABLE SHOWING THE AMOUNT OF DISSOLVED OXYGEN AT VARIOUS DEPTHS IN CERTAIN PONDS AND RESERVOIRS IN MASSACHUSETTS. COMPILED FROM THE REPORTS OF THE MASSACHUSETTS STATE BOARD OF HEALTH, THE ANNUAL REPORTS OF THE BOSTON WATER-WORKS, ETC.

POND	DATE	DEPTH IN FEET	TEMPERATURE CENTIGRADE	DISSOLVED OXYGEN
				Per cent of saturation
Jamaica Pond	June 11, 1891	0	25	100
		10	20	100
		20	20	80
		30	12	59
		40	12	11
		50	0
	June 25, 1891	57	0
		0	21.7	100
		35	5.8	37
		40	5.8	0
	July 14, 1891	50	5.6	0
		0	24.0	100
		10	23.8	100
		20	12.3	49
		30	5.8	29
		35	5.6	4
		40	5.4	0
		47	5.2	0
	Jan. 24, 1893 (surface frozen)	0	0	98
		10	2	100
		20	2.1	89
		30	2.2	72
		40	2.2	19
		44	2.2	0
Lake Cochituate	Aug. 17, 1891	0	23.6	79
		10	19.1	84
		20	12.1	36
		30	9.6	21
		40	9.1	21
		45	9.1	2
		50	7.6	0
		57	7.1	0
	Feb. 14, 1893 (surface frozen)	0	0	100
		10	3.8	100
		20	2.8	100
		30	2.8	94
		40	2.8	83
		45	2.8	60
		50	2.9	49
		55	2.9	37
	Sept. 18, 1890	0	21.0	97
		15	21.0	88
		30	10.0	20
		40	9.4	12
		50	7.7	0
		60	7.5	0

TABLE VII—*Continued*

POND	DATE	DEPTH IN FEET	TEMPERA- TURE CEN- TIGRADE	DISSOLVED OXYGEN
				Per cent of saturation
Lake Cochituate.....	Sept. 28, 1891	0	21.0	90
		10	14.0	81
		20	14.5	33
		30	11.0	9
		40	11.0	8
		50	10.0	0
		56	9.0	0
Mystic Lake	March 8, 1893 (surface frozen)	0	0	60
		10	1.2	64
		20	2.1	68
		30	2.2	58
		40	2.2	55
		50	2.2	50
		54	2.4	49
		60	2.4	43
		64	2.4	25
		66	2.7	13
		68	2.7	0
		74	2.7	0
Reservoir No. 4, Boston.....	Aug. 20, 1891	0	23.6	85
		10	21.6	84
		20	16.6	28
		30	27
		35	12.6	16
		36½	12.6	15
		0	0	100
	Feb. 14, 1893 (surface frozen)	10	3.4	100
		20	3.8	92
		25	3.9	78
		30	3.7	60
	Sept. 25, 1890	0	18.2	92
		10	18.0	87
		20	15.9	18
		29	12.3	7
	Oct. 1, 1891	0	22.0	88
		10	21.5	84
		15	21.0	83
		20	15.0	9
		25	14.5	7
		31	12.0	4
Reservoir No. 3, Boston.....	Aug. 20, 1891	0	23.6	86
		6	23.6	85
		12	21.6	59
		14	0
		15	0
		17	0
		19	0
		21	17.1	0
	Jan. 30, 1893 (surface frozen)	0	2.2	81
		5	2.1	62
		10	2.1	45

TABLE VII—*Concluded*

POND	DATE	DEPTH IN FEET	TEMPERATURE CENTIGRADE	DISSOLVED OXYGEN
				Per cent of saturation
Reservoir No. 3, Boston.....	Jan. 30, 1893	14	2.3	44
Reservoir No. 2, Boston.....	Jan. 30, 1893	0	1.2	86
	(surface	5	1.3	79
	frozen)	10	1.5	32
Scott Res., Fitchburg.....	July 29, 1891	0	21.4	87
		10	18.8	79
		20	16.2	32
		25	10.2	11
		30	0
		35	0
Glenn Lewis Pond, Lynn	June 26, 1891	0	24.2	100
		5	100
		7	100
		10	0
		13½	17.2	0
	Jan. 26, 1893	0	2.8	7
	(Surface frozen)	5	3.3	6
Walden Pond, Lynn.....	Jan. 26, 1893	0	3.8	64
	(surface	5	3.8	26
	frozen)	10	3.5	20
		15	2.8	24
Brocton Reservoir.....	Mar. 15, 1893	0	0	90
	(surface	5	3.0	80
	frozen)	10	4.0	60
		12	3.9	28
		14	3.9	20
		16	3.9	4
		18	3.9	0
Van Horn Res., Springfield..	July 16, 1891	0	24.1	100
		7	24.1	100
		14	24.1	46
		17	0
		20	0
		28	0

TABLE VIII

TABLE SHOWING THE AMOUNT OF DISSOLVED OXYGEN IN CERTAIN OHIO
RIVER WATERS

SCIOTO RIVER

STATION	DATE	TEMPERATURE CENTIGRADE	DISSOLVED O ₂ % SATUR- ATION
Kenton, above town.....	June 12....		
	July 16....	25.5	91
	Aug. 25....	21	85
	Sept. 25....	16	84
	Oct. 23....	15	114
	Dec. 1....	4	84
Kenton, below town.....	June 12....		
	July 16....	25	114
	Aug. 25....	23.5	169
	Sept. 25....	18.5	72
	Oct. 23....	16.5	159
	Dec. 1....	3.75	90
Girls' Industrial Home, above.....	Oct. 7....	17.5	106
	Oct. 26....	15.5	99
	Dec. 2....	2.5	94
Girls' Industrial Home, below.....	Oct. 7....	17	113
	Oct. 26....	17	116
	Oct. 26....	17	118
	Dec. 2....	3	
Wyandotte Grove.....	Dec. 2....	3	91-93
	June 13....		
	June 17....	27	103
	Aug. 23....	23	83
	Sept. 23....	17	89
	Oct. 21....	16	79
Jours Dam.....	Dec. 3....	2.5	85
	June 13....		
	July 17....	25.5	93
	Aug. 23....	23	101
	Sept. 23....	19	86
	Oct. 21....	16	73
Columbus, Sandusky St. Bridge.....	Dec. 3....	2.5	86
	June 13....		
	July 17....	27.5	118
	Aug. 23....	22.5	42
	Sept. 23....	20	91
	Oct. 21....	16	96
Columbus, Frank Rd. Bridge..... (below sewers)	Dec. 3....	3	89
	July 17....	23.5	9
	Aug. 23....	23	21
	Sept. 23....	19.5	0
	Oct. 21....	17	0
	Dec. 4....	5	78
Shadeville Bridge..... (apparently below town)	July 17....	23	46
	Aug. 23....	22.5	100
	Sept. 23....	19	58
	Oct. 22....	17	0
	Dec. 4....	4.5	81

TABLE VIII—*Continued*
SCIOTO RIVER—*Continued*

STATION	DATE	TEMPERATURE CENTIGRADE	DISSOLVED O ₂ % SATUR- ATION
Cuchville, Main St. Bridge.....	July 22...	26	57
	Aug. 26...	22.5	57
	Sept. 27...	18	71
	Oct. 25...	14	32
	Dec. 4...	6	59
LITTLE SCIOTO RIVER			
Marion, above town	July 15...	26	116
	Aug. 24...	23	114
	Sept. 24...	20	50
	Oct. 23...	11	50
	Dec. 1...	1	82
Marion, below town	July 15...	26	1125
	Aug. 24...	23	46
	Sept. 24...	21	61
	Oct. 23...	11.2	72
	Dec. 1...	2	27
CLETANGY RIVER			
Galion, above town.....	July 15...	22.5	147
	Aug. 24...	22.5	123
	Sept. 24...	21	107
	Oct. 22...	12	74
	Nov. 30...	3	90
Galion, below town.....	July 15...	24	51
	Aug. 24...	20	36
	Sept. 24...	18	77
	Oct. 22...	13	0
	Nov. 30...	4	72
Delaware, above town	July 15...	22	87
	Aug. 24...	21	76
	Sept. 24...	15	84
	Oct. 26...	14	87
	Dec. 2...	1	82
Delaware, below town	July 15...	24	91
	Aug. 24...	19	71
	Sept. 24...	13	79
	Oct. 26...	14	99
	Dec. 2...	2.5	89
Cletangy Park, above.....	July 16...	24.5	85
	Aug. 24...	22.5	80
	Sept. 23...	17	74
	Oct. 21...	15.5	61
	Dec. 3...	3	83
Columbus, Dublin Bridge.....	July 17...	27	109
	Aug. 23...	23	97
	Sept. 23...	21	129
	Oct. 21...	16.2	93
	Dec. 3...	3	89

TABLE VIII—*Concluded*

MAHONING RIVER

STATION	DATE	TEMPERATURE CENTIGRADE	DISSOLVED O % SATUR- ATION
Alliance, above Pat. St. Bridge.....	July 24...	23	66
	Sept. 2...	23	94
	Sept. 29...	19	97
	Oct. 27...	14	80
	Nov. 26...	11	81
Alliance, below.....	July 24...	25	75
	Sept. 2...	25	81
	Sept. 29...	19	70
	Oct. 27...	16	35
	Nov. 26...	8	90
Warren, above.....	July 23...	23	68
	Aug. 28...	23.5	99
	Sept. 30...	16	90
	Oct. 28...	13	82
	Nov. 27...	7	83
Warren, below.....	July 23...	23	76
	Aug. 28...	23	66
	Sept. 30...	16	72
	Oct. 28...	14	54
	Nov. 27...	8	90
Niles.....	July 24...	23	70
	Aug. 28...	21.5	92
	Sept. 30...	15	89
	Oct. 28...	13	70
	Nov. 27...	8	81
Youngstown, above.....	July 23...	21.5	86
	Aug. 28...	26	82
	Sept. 30...	20.5	93
	Oct. 28...	16	76
	Nov. 27...	7.5	90
Haselton Bridge.....	July 23...	21.5	72
	Aug. 28...	26	65
	Sept. 30...	22	77
	Oct. 28...	18	51
	Nov. 27...	7	84

The amount of dissolved oxygen in certain river waters of Ohio as given above in Table VIII, is taken from the *Thirteenth Annual Report of the State Board of Health*.

The tap water in most towns and cities where surface supplies are used is usually well aerated, as shown in Table IX, but in the case of water rich in organic matter or in micro-organisms a loss of oxygen sometimes occurs in the pipes of the distribution system, as Table X illustrates.

TABLE IX

TABLE SHOWING THE AMOUNT OF DISSOLVED OXYGEN IN THE PUBLIC WATER-SUPPLIES OF CERTAIN MASSACHUSETTS CITIES AND TOWNS WHERE SURFACE WATER IS USED. COMPILED FROM REPORT FROM MASS. ST. BD. OF HEALTH FOR 1898, P. 367

CITY OR TOWN	DISSOLVED OXYGEN (Per cent of saturation)
Boston	84
Stoughton	73
New Bedford.....	54
Norwood.....	100
Palmer.....	92
Chicopee.....	97
Lawrence	85
Concord	75
Fall River.....	98
Rockland	83
Springfield.....	97

TABLE X

TABLE SHOWING THE DECREASE IN THE AMOUNT OF OXYGEN IN THE PIPES OF A WATER-WORKS DISTRIBUTION SYSTEM. COMPILED FROM MASS. ST. BD. OF HEALTH REPT. 1891, P. 379

			TEMP.	DISSOLVED OXYGEN Per cent of saturation
Large Ludlow res., Springfield, Mass.	Surface	July 16, 1891	24.1° C.	98
Large Ludlow res., Springfield, Mass.	Bottom.	July 16, 1891	23.6	61
Small Ludlow res., Springfield, Mass.	Surface	July 16, 1891	24.1	78
Small Ludlow res., Springfield, Mass.	Bottom.	July 16, 1891	23.6	71
Tap after passing through 6 miles of pipe.....	July 16, 1891	23.6	61
Tap after passing through 9 miles of pipe.....	July 16, 1891	23.6	57

The amount of dissolved oxygen in ground waters may vary from 0 to 100 per cent of saturation, and depends upon the character of the material with which the water comes in contact during its passage through the ground. If it meets decaying organic matter at the surface of the ground, or deposits of peat at greater depths, the oxygen may be used up, and especially is this true if iron is present with the organic matter. Table XI gives the amount of dissolved oxygen in certain ground water supplies of Massachusetts.

TABLE XI

TABLE SHOWING THE AMOUNT OF DISSOLVED OXYGEN IN CERTAIN DRIVEN WELL WATERS OF MASSACHUSETTS. COMPILED FROM REPT. MASS. ST. BD. HEALTH, 1898, P. 566

TOWN OR CITY	DISSOLVED OXYGEN (Per cent of saturation)
Lowell.....	10
North Easton.....	64
Fairhaven.....	47
Kingston.....	85
Sharon.....	93
Milford.....	49
West Brookfield.....	100
Framingham.....	43
South Hadley.....	100
Ashburnham.....	100
Revere.....	11
Malden.....	54
Methuen.....	9
Reading.....	100

AMOUNT OF FREE CARBONIC ACID IN NATURAL WATERS UNDER
VARIOUS CONDITIONS

The carbonic acid dissolved in surface waters is derived partly from the atmosphere and partly from the products of vital activity of organisms living in the water.

The amount of carbonic acid in the atmosphere is not a constant quantity. In pure sea air it may be as low as 0.02 per cent (2 parts in 10,000), while in the vicinity of cities it may be 0.05 per cent (5 parts in 10,000). In well-ventilated rooms it should not rise above 0.05 per cent (5 parts in 10,000), but when the ventilation is poor it rises to 0.2 per cent or 0.3 per cent (20 or 30 parts per 10,000), and in crowded rooms where gas is burning it may be even more than this. Out of doors it is generally somewhat higher in summer than in winter, because of the greater activity of organic life. It is usually lower after a rain. The vapor pressure of atmospheric carbonic acid is not ordinarily sufficient to permit a large amount to be present in solution in water exposed to the air, but as the free carbonic acid in the water is used up the loss is continually supplied from the atmosphere, so that at times the actual quantity given up by the atmosphere may be very considerable.

TABLE XII

TABLE SHOWING THE AMOUNT OF FREE CARBONIC ACID IN RAIN WATER
(IN PARTS PER MILLION)

LOCALITY	DATE	CARBONIC ACID	REMARKS
Brooklyn, N. Y...	Aug. 1, 1901	6.3	Latter part of a heavy shower.
Brooklyn, N. Y...	Aug. 7, 1901	2.7	At end of a long rain.
Boston, Mass.....	Sept. 18, 1901	6.0	At 1 Ashburton Place.
Boston, Mass.....	Oct. 14, 1901	8.0	At 1 Ashburton Place, 11:30 A.M.
Boston, Mass.....	Oct. 14, 1901	5.0	At 1 Ashburton Place, 2:45 P.M.
Boston, Mass.....	Oct. 14, 1901	5.0	At 1 Ashburton Place, 4:15 P.M.
Boston, Mass.....	Oct. 15, 1901	9.0	At 1 Ashburton Place, 9:00 A.M.
Boston, Mass.....	Oct. 17, 1901	29.0	At 1 Ashburton Place, after sudden shower which lasted $\frac{3}{4}$ hour.
Cambridge, Mass..	Sept. 29, 1901	5.0	After three hours' fall.
Fitzwilliam, N. H.	Sept. 1, 1901	2.5	At beginning of shower, in country.
Fitzwilliam, N. H.	Sept. 1, 1901	1.8	At end of shower, in country.

Rain water contains carbonic acid in amounts corresponding to those present in the atmosphere. In the vicinity of cities it is sometimes as high as 20 or 30 parts per million, but where the air is purer it is seldom higher than 3 or 4 parts. Rain at the end of a long storm contains less carbonic acid than at the beginning. This is illustrated by Table No. XII. If rain water is allowed to stand in a shallow receptacle out of doors it will lose much of its carbonic acid in the course of a few hours and the loss will proceed until equilibrium with the carbonic acid of the atmosphere is established.

Most of the carbonic acid found in surface waters is not derived directly from the atmosphere by absorption nor by accession of rain-water, but its chief source is to be sought in the living organisms which inhabit the water. All animals exhale carbonic acid, and under certain conditions chlorophyllaceous plants do likewise, but it is chiefly to the bacteria that we look to find this action. These minute plants, countless in number and of enormous aggregate power, are continually breaking down nitrogenous organic matter or fermenting carbohydrates, with the consequent liberation of carbonic acid. In many of these vital processes oxygen and carbonic acid appear to act reciprocally: at one time oxygen is taken in and carbonic acid given out, while at another time carbonic acid is used up and oxygen liberated.

The production of carbonic acid by bacterial action scarcely needs illustration. The fermentation of the sugars in the absence of oxy-

gen has come to be a common differential test in bacteriological laboratories, the observed data including the total amount of gas produced and the percentage which the carbonic acid is of the total gas. Thus in the closed arm of the fermentation tube the common colon bacillus produces enough gas to occupy about 50 per cent of the volume of the tube, and of this about one-third is carbonic acid. Other bacteria produce still greater amounts. As a rule the anaerobic bacteria produce larger amounts than do the aerobic forms, a fact which accounts for the accumulation of carbonic acid at the bottom of stagnant ponds. Yeasts, molds, and other fungi also produce carbonic acid, and no doubt these play an important part in nature. In general it may be said that wherever decomposition is going on in water there is carbonic acid going into solution, and the larger the amount of organic matter and the more numerous the bacteria the greater is the amount of carbonic acid dissolved.

TABLE XIII

TABLE SHOWING THE AMOUNT OF FREE CARBONIC ACID IN SURFACE WATERS EXPOSED TO THE ATMOSPHERE (IN PARTS PER MILLION)

SOURCE	DATE	CARBONIC ACID	REMARKS
STREAMS OF METROPOLITAN WATER-WORKS, BOSTON, MASS.			COLOR
Influent to Framingham Res. No. 2	Oct. 23, 1901	6.0	140
	Oct. 30, 1901	7.0	126
	Nov. 6, 1901	5.0	86
	Nov. 20, 1901	5.2	74
	Nov. 26, 1901	5.0	83
Influent to Sudbury Res.	Oct. 23, 1901	5.0	67
	Oct. 30, 1901	5.0	54
	Nov. 21, 1901	3.6	41
Deerfoot Brook	Oct. 17, 1901	8.0	176
Rock Meadow Brook	Oct. 17, 1901	8.0	148
Angelico Brook	Oct. 17, 1901	4.0	130
Brewer Brook	Oct. 17, 1901	8.0	82
Mowry Brook	Oct. 17, 1901	5.0	69
Brown Meadow Brook	Oct. 17, 1901	5.0	49
Cold Spring Brook	Oct. 15, 1901	8.0	145
	Oct. 22, 1901	8.0	188
	Oct. 29, 1901	8.0	200
	Nov. 19, 1901	5.4	118
	Nov. 26, 1901	6.8	110
Indian Brook	Oct. 15, 1901	19.0	212
	Oct. 22, 1901	14.4	204
	Oct. 29, 1901	15.0	180
	Nov. 12, 1901	16.0	128

TABLE XIII—*Continued*

SOURCE	DATE	CARBONIC ACID	REMARKS
STREAMS OF METROPOLITAN WATER-WORKS, BOSTON, MASS.			
Indian Brook.....	Nov. 19, 1901	14.6	COLOR 120
Course Brook.....	Oct. 4, 1901	10.0
	Oct. 11, 1901	9.0	82
	Oct. 29, 1901	6.01	94
Pegan Brook.....	Oct. 4, 1901	4.0
	Oct. 11, 1901	5.0	7
	Oct. 29, 1901	4.0	4
Beaver Dam Brook.....	Oct. 4, 1901	10.0
	Oct. 11, 1901	9.0	125
	Oct. 29, 1901	6.0	122
Snake Brook.....	Oct. 29, 1901	10.0	66
Nashua River, S. Br., Clinton, Mass.	Nov. 8, 1901	5.0	
Lancaster, Mass.	Nov. 8, 1901	9.2	
" N. Br., Lancaster, Mass.	Nov. 8, 1901	6.6	
Pepperell, Mass.	Nov. 7, 1901	7.6	
OTHER STREAMS.			
Beaver Brook, Waverly, Mass.	Oct. 13, 1901	5.6	105
Kemp Brook, Fitzwilliam, N. H.	Sept. 6, 1901	8.0	Approx- imately } 150
Hempstead Stream, L. I.	Sept. 5, 1900	2.0	15
Schodack Brook, L. I.	Sept. 5, 1900	5.7	12
	Sept. 8, 1900	3.0	10
	Sept. 15, 1900	2.5	18
SHALLOW PONDS.			
Average of 15 shallow ponds on Long Island during summer of 1900.....	3.0	Av. depth about 6 ft., and av. color about 30
Laurel Lake, Fitzwilliam, N. H.	Sept. 6, 1901	1.5	
Boston Public Gardens Pond.....	Oct. 17, 1901	2.0	
Frog Pond, Boston Common.....	Oct. 18, 1901	7.0	
	Oct. 19, 1901	5.0	
	Oct. 21, 1901	5.0	
	Oct. 22, 1901	5.0	
	Oct. 23, 1901	6.0	
	Oct. 24, 1901	6.0	
	Oct. 25, 1901	5.0	
	Oct. 29, 1901	6.0	
Farm Pond S. Framingham, Mass.	Nov. 15, 1901	2.0	
Nissitisset River, Pepperell, Mass..	Nov. 7, 1901	6.0	

In surface waters which are exposed to the atmosphere and contain but little organic matter, the amount of free carbonic acid usually varies from 2 to 5 parts per million. In Brooklyn, N. Y., the average amount in the tap water is 4 parts per million; in Boston it is about 2 or 3 parts per million; in Cambridge, Mass., about 5 parts. In Table XIII will be found the amounts of carbonic acid in various

streams and shallow ponds. It has been found that in a general way the amount of carbonic acid increases with the color of the water, but this is not always the case. Pollution usually increases the amount of carbonic acid present. For example, a stream which flows through the town of Hempstead, L. I., contained on September 6, 1900, 2 parts per million above the town and 9 parts per million below it.

TABLE XIV

TABLE SHOWING THE AMOUNT OF CARBONIC ACID AT VARIOUS DEPTHS IN DEEP PONDS AND RESERVOIRS

POND OR RESERVOIR	DATE	DEPTH IN FT.	CARBONIC ACID (parts per mill'n)	REMARKS
Chestnut Hill Reservoir	Sept. 20, 1901	1	3.0	
		13	3.0	
		26	11.0	
	Sept. 23, 1901	1	2.0	
		13	2.0	
		26	9.0	
	Sept. 30, 1901	1	2.0	
		13	2.0	
		25	6.0	
	Oct. 15, 1901	1	2.0	
		12	2.0	
		24	4.0	
	Oct. 21, 1901	1	2.0	
		12	2.0	
		24	2.0	
	Nov. 4, 1901	1	4.0	
		2	2.0	
		24	2.0	
	Nov. 8, 1901	1	3.4	
		2	6.2	
		24	6.2	
	Nov. 18, 1901	1	3.0	
		2	3.0	
		24	5.0	
Hopkinton Res.....	Oct. 29, 1901	1	4.0	After autumnal over- turning.
		26	4.0	
		52	4.0	
Framingham Res. No. 3.	Nov. 15, 1901	1	3.0	
Sudbury Res.....	Nov. 15, 1901	1	4.0	
Spot Pond.....	Dec. 6, 1901	1	1.4	
		12	7.0	
		24	8.0	
Fells Res. G. H.....	Dec. 6, 1901	3.6	
Fresh Pond, Cambridge..	Sept. 28, 1901	1	1.0	
		23	8.0	
		46	16.0	

The amount of dissolved carbonic acid found in a shallow surface water depends, however, upon other factors than those which cause its formation. It is always complicated by reason of its reaction with the normal carbonates of the alkaline earths with which it may come in contact, and there is usually a tendency for it to diffuse into the atmosphere. This diffusion depends upon the vapor pressure of the atmospheric carbonic acid and the extent to which the water is exposed to the air. In the middle of swamps which are covered with tall vegetation to such an extent that the air does not circulate freely the carbonic acid is often high in the air and in the water in contact with it. At the bottom of thermally stratified ponds there is no opportunity for the water to come in contact with the atmosphere, and consequently there is often a concentration of carbonic acid in the lower strata. This is especially true if there are deposits of mud and organic matter at the bottom. (See tables XIV, XV, and XVI.)

TABLE XV

TABLE SHOWING THE AMOUNT OF FREE CARBONIC ACID AT DIFFERENT DEPTHS IN LAKE COCHITUATE (IN PARTS PER MILLION)

DEPTH IN FT.	1900 OCT. 12	1900 NOV. 9	1900 ⁹ NOV. 16	1901 MAY 24	1901 JUNE 21	1901 JULY 19	1901 AUG. 28	1901 OCT. 11	1901 NOV. 8	1901 ¹⁰ NOV. 14
1	2.0	2.8	3.6	1.6	2.0	2.0	2.0	2.6	4.0	6.0
5	2.2	3.0	3.6
10	2.25	2.8	2.0	5.6	3.0	2.0	3.0	4.0
15	2.25	2.8	5.2	5.6	6.0	5.0	4.0	4.0
20	2.30	2.8	6.8	6.0	6.0	6.0	10.0	4.0
25	9.4	3.2	6.0	6.0	6.0	6.0(26 ft.)
30	9.15	4.0	6.0	6.0	6.0	6.0	11.0	4.0
35	9.55	5.4
40	11.0	15.6	10.0	6.0	6.0	7.0	11.0	7.0
45	11.65	18.5
50	17.50	16.6	3.7	8.0	9.6	8.0	8.0	19.0	21.0
55	10.0	16.0	23.0	6.0(52 ft.)
60	8.0	12.0	12.0	16.0	23.0	24.0

The phenomena which take place at the bottom of a thermally stratified lake are most interesting. Below the thermocline the water is shut off from communication with the atmosphere. The processes of vital activity soon cause a diminution in the amount of dissolved oxygen and an increase in the amount of free carbonic

⁹ The lake overturned on Nov. 12, 1900.

¹⁰ The lake overturned on Nov. 10, 1901.

acid. If there is a deposit of organic matter at the bottom the oxygen may become entirely exhausted, after which decomposition may occur under anaerobic conditions. The anaerobic bacteria are vigorous producers of carbonic acid, and consequently a large amount of this gas goes into solution. The carbonic acid also unites with the iron present at the bottom, forming soluble ferrous carbonate. This gives rise to an increased color and turbidity of the water, which, on exposure of the water to the air, is still further increased by the oxidation and precipitation of the iron. Under the conditions which thus prevail at the bottom of a stagnant lake *Crenothrix* may develop. After the period of stratification ceases and circulation takes place through the vertical, the products of decomposition become distributed through the entire body of water. These phenomena are well illustrated by observations made at Lake Cochituate, and given in Table XV. See also Plates XXI and XXII.

TABLE XVI

TABLE SHOWING THE AMOUNT OF CARBONIC ACID AT VARIOUS DEPTHS IN A SMALL DISTRIBUTION RESERVOIR IN WHICH GROUND WATER IS STORED, TOGETHER WITH THE TEMPERATURE AND THE NUMBER OF MICROSCOPIC ORGANISMS PER C.C.

SEPTEMBER 4, 1900				JULY 25, 1901			
Depth	Temperature (Fahr.)	Amt. of free carbonic acid in parts per million	No. of microscopic organisms per c.c. ¹¹	Depth	Temperature (Fahr.)	Amt. of free carbonic acid in parts per million	No. of microscopic organisms per c.c. ¹²
0	80.0	0.0	0	79.5	—5.0	5760
2	79.5	0.0	140	2	79.5	—5.0
4	79.5	0.0	4	79.0	—5.0
6	79.5	0.0	6	79.0	—5.0	6900
8	79.5	0.0	225	8	78.0	—5.5	2760
10	78.0	0.5	430	10	78.0	1.5
12	77.0	1.0	3575	12	77.5	1.5	800
14	76.5	1.5	2990	14	77.0	3.0
16	76.5	1.5	3610	16	76.5	4.0
18	75.5	2.5	4480	18	75.5	5.0
20	74.0	4.0	5660	20	75.5	6.0	600

In testing surface waters for carbonic acid it sometimes happens that a negative result is obtained; that is, the water is alkaline to phenolphthalein and requires the addition of a certain amount of acid to make it neutral. This phenomenon is generally associated with the presence of microscopic organisms, as referred to below. (See Table XVI.)

¹¹ Chiefly *Melosira* and *Synedra*.

¹² Chiefly *Scenedesmus*.

The amount of free carbonic acid in ground water is generally higher than in surface waters. This may be seen by an inspection of Tables XVII, XVIII, and XIX.

TABLE XVII

TABLE SHOWING THE AMOUNT OF FREE CARBONIC ACID IN VARIOUS DRIVEN WELLS ON LONG ISLAND

WELL	DATE	CARBONIC ACID (Pts. per mil.)
Gravesend, driven wells.....	August 20, 1900..	2.4
New Utrecht, driven wells.....	July 20, 1901..	4.0
Flatbush, driven wells.....	August 31, 1900..	5.5
Pfalzgraf, driven wells.....	August 31, 1900..	9.2
Blythebourne, driven wells.....	August 31, 1900..	1.5
Far Rockaway, driven wells, before filtration..	August 25, 1900..	5.3
after filtration..	August 25, 1900..	6.6
Long Island City, Station 1.....	September 6, 1900..	1.0
2.....	September 6, 1900..	3.5
3.....	September 6, 1900..	2.5
Jamaica Water-supply Co.....	September 7, 1900..	6.0
Montauk Water-works.....	September 7, 1900..	6.5
German-America Water-supply Co.....	September 7, 1900..	2.0
Woodhaven P. S.....	September 8, 1900..	3.0
Flushing Water-works.....	September 10, 1900..	7.0
College Point Water-works.....	September 10, 1900..	6.0
Oconee driven wells.....	September 14, 1900..	2.0
Shetucket driven wells.....	September 14, 1900..	7.0
Jameco driven wells.....	8.0
Springfield driven wells.....	September 17, 1900..	12.0

In dug wells the amount of carbonic acid is often higher than in driven wells. It varies, however, with the character of the water, the character of the soil, the amount of ventilation, etc. A poorly ventilated well of good water may be higher in carbonic acid than a perfectly ventilated well of polluted water, but as a rule the extremely high figures for carbonic acid are obtained from polluted wells.

THE RELATION OF DISSOLVED OXYGEN AND CARBONIC ACID TO THE OCCURRENCE OF THE MICROSCOPIC ORGANISMS IN WATER

One of the great biological problems of the present time is to ascertain how the growth of the floating microscopic organisms, the plankton, may be controlled. Inasmuch as these organisms are the basis of the food-supply of fish and aquatic animals, it is

desirable to know how to cultivate them, but as their presence gives rise to unpleasant odors and turbidities in drinking waters it is desirable to prevent their growth in reservoirs and lakes used for public supplies.

TABLE XVIII

AMOUNT OF FREE CARBONIC ACID IN MASSACHUSETTS GROUND WATERS ¹³
(IN PARTS PER MILLION)

LOCATION	PARTS PER MILLION
Driven wells at Lowell	28.5
North Easton	23.4
Fairhaven	21.7
Kingston	20.3
Sharon	19.6
Milford	15.5
West Brookfield	15.2
Framingham	15.1
South Hadley	9.2
Ashburnham	8.0
Revere	7.4
Malden	7.0
Methuen	2.9
Brookline (Seyler's method)	13.0 ¹⁴
Newton (Seyler's method)	16.0 ¹⁵

NOTE.—These results were obtained by using Drown's modification of the Pettinkofer method, by which the combined, free, and half-bound carbonic acid is determined before and after passing the sample through a tube filled with coarse gravel, the free carbonic acid being obtained by difference. The results are not strictly comparable with the results obtained by Seyler's method.

TABLE XIX

TABLE SHOWING THE AMOUNT OF FREE CARBONIC ACID IN THE WATER OF
CERTAIN DUG WELLS IN FITZWILLIAM, N. H., AUG. 26, 1901.

WELL	CARBONIC ACID	REMARKS
No. 1....	13.2	A shallow well with good ventilation.
2....	16.1	Deep well, fairly well ventilated.
3....	30.8	Deep well, poorly ventilated.
4....	33.8	Deep well, fairly well ventilated.
5....	33.9	Shallow well, very poorly ventilated.

¹³ H. W. Clark, *Rept. Mass. St. Bd. of Health*, p. 566. 1898.

¹⁴ By the authors, Nov. 18, 1901. ¹⁵ By the authors, Nov. 19, 1901.

Although much study has been given to this subject, and although it has been approached from many standpoints of bio-chemistry and bio-physics it is for the most part still unsolved. The relation of the micro-organisms to the oxygen contents of waters has been investigated, but their relation to dissolved carbonic acid has received scant attention, probably because of the elusive nature of this gas in water and the difficulty of determining its amount. Inasmuch as the algae and many of the troublesome protozoa are chlorophyl-bearing, the relation is one of fundamental importance. All such organisms require both oxygen and carbonic acid in their metabolic processes.

It has been shown that all bodies of water exposed to the air have what may be called a respiration. At times they breathe in oxygen and emit carbonic acid; less often they take in carbonic acid and give out oxygen. There is a continual adjustment taking place between the gases dissolved in the water and the gases present in the atmosphere, and when all the facts which enter into this transfer of oxygen and carbonic acid are known a long step will be taken towards solving the problem of the occurrence of the microscopic organisms.

Certain inferences may be drawn from the data now at hand. For some years it has been a well-recognized fact that ground water stored in an open reservoir is liable to become infested with troublesome algae growths, particularly with diatoms such as *Asterionella*, *Synedra*, *Melosira*, etc. The explanation given for this is chiefly based on the nitrogen content of the water. It is known that ground waters are usually rich in nitrates. That this form of nitrogen is readily assimilated by plants is shown by the fact that exhaustion of nitrates occurs in ground water supporting a vigorous growth of algae in the sunlight. Hence, it was assumed that nitrates are the fundamental factor in the development of the algae. Nitrates are indeed important, but the inadequacy of this explanation became manifest when it was observed that some water, comparatively low in nitrates, at times supported large growths of algae. Another reason for the development of algae in ground water suggests itself, namely, the presence of carbonic acid. Its occurrence in comparatively large amounts in waters of this class has been shown, and there is good reason to believe that the algae are influenced by it more than by the nitrates, although of course the latter are necessary.

The consumption of carbonic acid by diatoms has found illustration in several recent instances where *Asterionella* and *Synedra* have developed in ground waters exposed to the light. At the inlet of a certain reservoir where *Asterionella* were abundant the water contained five to eight parts per million of carbonic acid, while at the outlet it was entirely absent.

Again, in explaining the occurrence of diatom growths in the spring and autumn, immediately after the overturning of the water, carbonic acid has been largely ignored. We know that decomposition takes place in the lower strata of ponds which have deposits of organic matter at their bottoms and that the overturning brings the products of decomposition to the surface, where the nitrogen as free ammonia is oxidized to nitrates. In this form it is readily assimilated by the diatoms, which also are carried upward by the vertical currents to the region where they receive the necessary amount of sunlight for their growth. But we have not appreciated that a large amount of carbonic acid is simultaneously distributed through the water. But such is the case, and at the surface the chlorophyl-bearing organisms, under the influence of the sunlight, break down the carbonic acid, store up carbon, and assimilate oxygen. It is quite possible that the duration of their growth is determined by the amount of carbonic acid present, but observations upon this point are not convincing.

As a rule, growths of diatoms are most vigorous near the surface of a pond, but in light colored water heavy growths occasionally occur at a depth of twenty or even thirty feet. Indeed, instances are on record where growths of *Melosira* and *Synedra* have started at the bottom and finally spread through the entire body of water. Such cases may be explained by the vertical distribution of the carbonic acid. Table XVI shows this. On September 14, 1900, *Melosira* and *Synedra* were present below the thermocline in the water of a small reservoir. At this time oxygen was abundant at all depths, but carbonic acid was present only near the bottom.

The normal distribution of diatoms is illustrated by the results obtained in the same reservoir on July 25, 1900. On this date, the organisms were very numerous near the surface, but were almost absent near the bottom. It will be observed that above the thermocline the water was alkaline to phenolphthalein, indicating the presence of a certain amount of normal carbonates in solution. This

alkalinity to phenolphthalein has been more frequently observed in connection with vigorous growths of the blue-green algae. It is possible that certain organisms under certain conditions have the power of taking carbonic acid from the hypothetical bicarbonates of the alkaline earths. This would accord with the fact noted long ago by one of the authors that, in Massachusetts water-supplies, heavy growths of organisms were somewhat more likely to occur in hard waters than in soft waters.

The presence of carbonic acid and oxygen at various depths throws light on another interesting problem of vertical distribution. It has been frequently noticed that some organisms at certain times of the year are most abundant, not at the surface or at the bottom, but at some point between the two,—generally just beneath the thermocline. They apparently shun the circulating water above and the stagnant water below. This is especially true of *Mallomonas*, attention to which was called by the writers in 1899.¹⁶ The following illustration may be cited:

On July 17, 1896, samples of water taken at different depths in Lake Cochituate contained the following numbers of *Mallomonas* per c.c.:

DEPTH	MALLOMONAS PER C.C.
0	0
10	0
15	2
20	1454
25	794
30	548
40	112
50	88
60	64

These figures, together with the corresponding temperatures, are shown at Plate XXII. It will be seen that the organisms were concentrated just below the thermocline. From what is now known of the distribution of oxygen and carbonic acid in Lake Cochituate, the reason for this is at hand. At the surface and throughout the circulating water above the thermocline, oxygen was abundant, but carbonic acid was absent. Near the bottom of the lake there was carbonic acid but no oxygen, and likewise an insufficient amount of light for plant growth. But just below the thermocline there was both carbonic acid and oxygen; and as *Mallomonas* is a chlorophyl-

¹⁶ See Whipple and Parker, "Note on the Vertical Distribution of *Mallomonas*," *The American Naturalist*, Vol. XXXIII, No. 390. June, 1899.

bearing organism it found there conditions favorable for its development.

Some of the blue-green algae likewise develop more vigorously at a slight depth in the water than they do at the immediate surface. This is illustrated by Plate XXI, which shows the vertical distribution of the blue-green algae in Lake Cochituate during the summer of 1901, together with the temperature and amount of carbonic acid at corresponding depths. It is noticeable that while *Anabaena* generally seeks the surface, *Aphanizomenon* is most abundant just above the thermocline. (See also Table XX.)

The knowledge of this relation of free carbonic acid to the growth of organisms is of especial interest to water-works managers, as it offers a chance of controlling the conditions. To some extent it has been unwittingly taken advantage of. The so-called process of aeration has been considered by some engineers and chemists to be instrumental in preventing growths of algae and protozoa; while others have adopted it without success. Much controversy has arisen accordingly over the merits of the process, and this has been due largely to a misconception of what takes place. So far as the actual oxidation of organic matter is concerned or any real purification of the water by the action of oxygen, there is little to be said in favor of the process. This was conclusively shown by Dr. T. M. Drown¹⁷ and by Dr. A. R. Leeds.¹⁸ But in its effect upon the growth of microscopic organisms it is not a question of oxygen so much as of carbonic acid, and any favorable result from the process comes, not so much from putting oxygen into the water, as from getting the carbonic acid out. The process may be said to be one of decarbonization rather than of aeration.

It has been shown that water rich in free carbonic acid loses much of this gas on exposure to the atmosphere. This takes place to some extent in nature. A water passing in a thin sheet over a dam, or falling over stones in broken streams loses a certain amount of carbonic acid, as illustrated by Table XXI. So also does well-water which is pumped into a reservoir in such a way that it falls in a broken column. But usually it is necessary to resort to some artificial device if it is desired to remove completely the carbonic acid. The water must be allowed to fall through the air in drops or in very

¹⁷ *Mass. St. Bd. of Health Rept.*, p. 385. 1891.

¹⁸ *Journal Am. Chem. Soc.* Nov., 1890.

TABLE XX

TABLE SHOWING THE VERTICAL DISTRIBUTION OF MICROSCOPIC ORGANISMS,
CARBONIC ACID, ETC., IN FRESH POND, CAMBRIDGE, MASS., ON
SEPTEMBER 28, 1901

	DEPTH, 1 FOOT	DEPTH, 23 FEET	DEPTH, 46 FEET
	Number of standard units per c.c.		
Carbonic acid, parts per million.....	1	8	16
Color, Platinum scale.....	26	48	180
Turbidity, silica scale.....	1.5	1.5	7
<i>Diatomaceae</i> —			
Asterionella.....	13	3
Cyclotella.....	3	1	14
Cymbella.....	5
Melosira.....	18	22	720
Navicula.....	8
Nitzschia.....	39	15	12
Stephanodiscus.....	12	6	96
Surirella.....	16
Synedra.....	596	115	180
Tabellaria.....
<i>Chlorophyceae</i> —			
Gonium.....	10
Protococcus.....	14
Raphidium.....	14
Staurostrum.....	98	33	24
Zoöspores.....	2
<i>Cyanophyceae</i> —			
Anabaena.....	850	120	20
Aphanizomenon.....	1,190	310
Clathrocystis.....	600	300	100
Coelosphaerium.....	1,320	570	880
Microcystis.....	14	26
<i>Schizomycetes</i> —			
Crenothrix.....	140	220
Beggiatoa.....	100
<i>Protozoa</i> —			
Arcella.....	24
Ceratium.....	180
Codonella.....	64
Cryptomonas.....	4
Mallomonas.....	4
Monas.....	1	1
Trachelomonas.....	4	8
Cercomonas.....	2	6
Coleps.....	10
<i>Rotifera</i> —			
Anuraea.....	60
Asplanchna.....	100
Polyarthra.....	80
Total organisms.....	5,228	1,718	2,482
Amorphous matter.....	60	280	320

thin sheets or streams. Several methods have been devised for doing this, and some of these have proved successful. For example, at West Superior, Wis., where a ground water is subjected to sand filtration for the purpose of removing the iron, there is an aerator consisting of two tiers of four trays each, spaced two feet apart vertically. The bottom of each tray is a steel plate $\frac{1}{4}$ -inch thick, punched with 3,900 $\frac{1}{4}$ -inch holes. The water from the pump discharges into a trough above the trays and flows downward through them, becoming thus fully aerated and losing practically all of its free carbonic acid. (See *Eng. News*, Feb. 21, 1901.)

TABLE XXI

TABLE SHOWING THE LOSS OF CARBONIC ACID FROM SURFACE WATERS BY NATURAL PROCESSES OF AERATION

LOCALITY	PLACE OF COLLECTION OF SAMPLE	DATE	CARBONIC ACID (Pts. per mil.)
Hopkinton Reservoir	At crest of dam	8-18-'01	4.0
	At foot of overflow	8-28-'01	2.0
Ashland Reservoir	At crest of dam	8-28-'01	2.6
	At foot of overflow	8-28-'01	2.0
	At crest of dam	11-15-'01	4.0
	At foot of overflow	2.4
Derby's Mill, Fitzwilliam, N. H.	At crest of dam	9- 6-'01	6.0 ¹⁹
	At foot of fall	9- 6-'01	5.0
Beaver Brook, Waverly, Mass.	Lower mill pond	10-13-'01	5.6
	After fall of 6 feet and run over 70 yards of rock	10-13-'01	3.8
	After a further fall of 9 feet and passage through a pool 5 feet wide	10-13-'01	3.0
	One-quarter mile below pool ..	10-13-'01	3.0 ²⁰
Fresh Pond, Cambridge...	Tap from pipe which supplies fountain	9-28-'01	3.0 ²¹
	Water falling from fountain...	9-28-'01	2.4 ²²
Framingham Res. No. 1...	At crest of dam	10-15-'01	3.0
	Below dam	10-15-'01	2.4
Nissitisset River, Peperell, Mass.	At dam	10- 7-'01	6.0
	After passing over dam	3.8

¹⁹ The fall is about 8 feet.

²¹ The fountain plays 15 feet into the air.

²⁰ Brook shallow, bottom sandy and stony.

²² Sample taken at bottom of fall.

RESUMÉ

In this paper the laws which govern the solution of gases in water are stated with special reference to oxygen and carbonic acid. Winkler's method for the determination of dissolved oxygen and a modification of Seyler's method for the determination of free carbonic acid are recommended as the most practicable and are fully described. The need of careful collection of samples and immediate treatment is emphasized. The amounts of oxygen and carbonic acid present in surface and ground waters are described and illustrated by tables. The effect of decomposing organic matter, sewage pollution, stagnation of deep lakes, etc., upon the gaseous contents of waters are given special attention. It is shown that bodies of surface water have what may be called a process of respiration, at one time taking in oxygen and giving out carbonic acid, and again inhaling carbonic acid and exhaling oxygen. The effect of this process upon the presence of the microscopic organism is then pointed out. It is shown how ordinarily both carbonic acid and oxygen are necessary to the life of the plankton, and how the presence or absence of one or both of these gases helps to explain certain problems of vertical and seasonal distribution. The relation between the high carbonic acid in ground waters and the peculiar tendency of such waters to support growths of diatoms is pointed out. Finally, natural and artificial methods of freeing a water of carbonic acid are discussed.

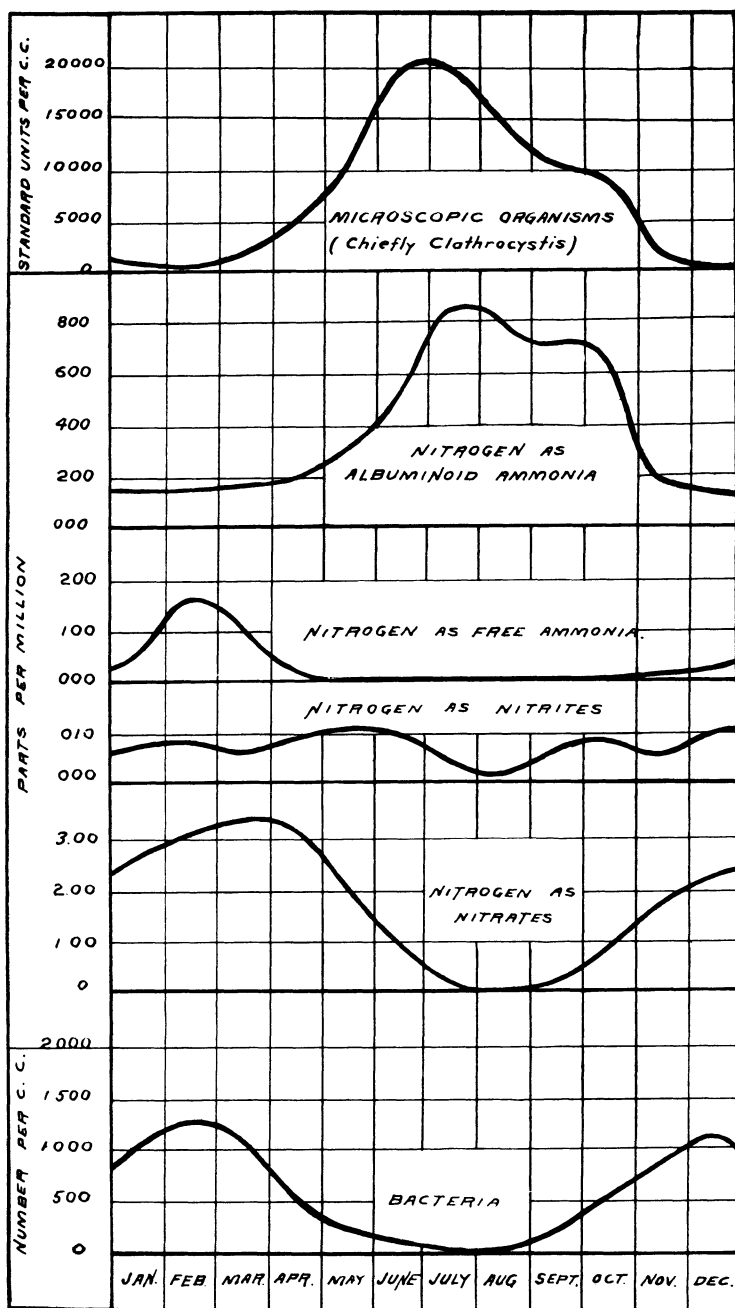


DIAGRAM SHOWING THE RELATION BETWEEN GROWTHS OF MICROSCOPIC ORGANISMS AND THE NITROGEN CONTENTS OF NATURAL WATERS.

PLATE XX

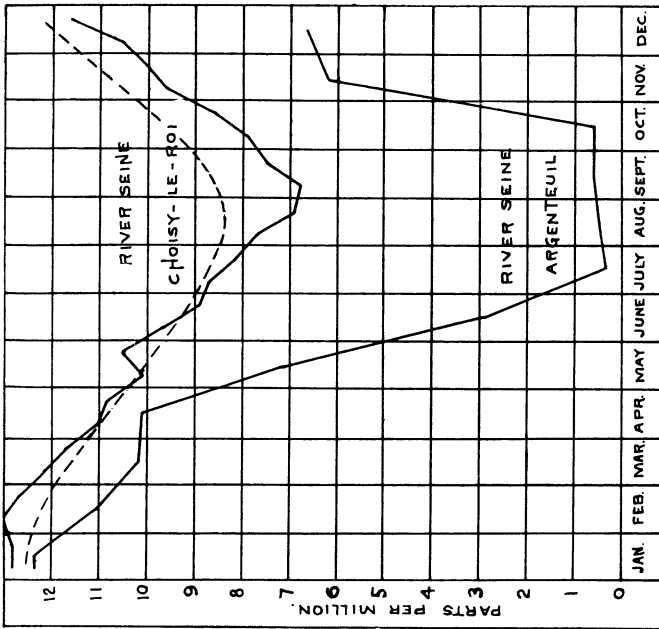


DIAGRAM SHOWING THE AMOUNT OF DISSOLVED OXYGEN IN THE WATER OF THE RIVER SEINE AT CHOISY-LE-ROI AND AT ARGENTEUIL DURING THE YEAR 1898. FROM ANALYSES BY M. ALBERT-LEVY. THE BROKEN LINE REPRESENTS SATURATION AT THE OBSERVED TEMPERATURES.

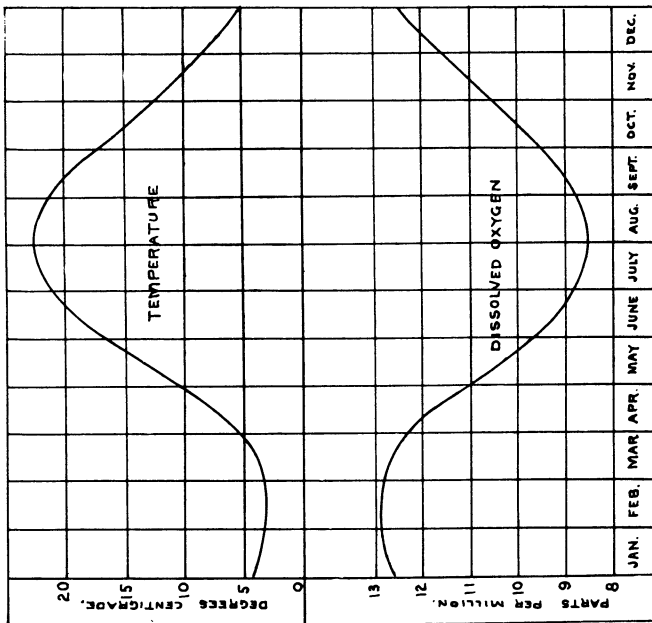


DIAGRAM SHOWING THE AVERAGE TEMPERATURE OF THE TAP WATER IN BOSTON, MASS. AND THE CORRESPONDING AMOUNT OF DISSOLVED OXYGEN WHEN THE WATER IS SATURATED.

PLATE XXI

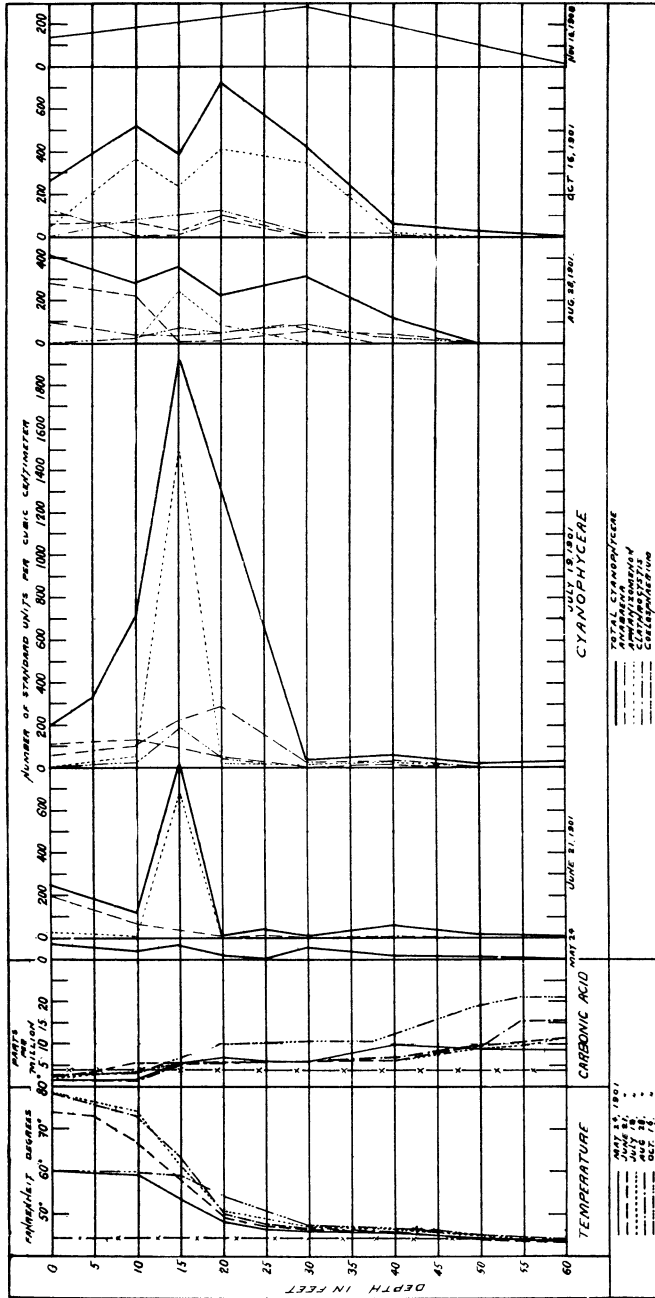


DIAGRAM SHOWING THE TEMPERATURE OF THE WATER THE AMOUNT OF FREE CARBONIC ACID AND THE NUMBER OF CYANOPHYCERE AT VARIOUS DEPTHS IN LAKE COCHITUATE

PLATE XXII

